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**(54) Polylactide with long-chain branching**

**(57) Polylactide homo or copolymers containing long-chain branchings**

Poly lactide is manufactured by ring-opening polymerization of lactide, with the configuration being retained. Poly-L and poly-D-lactides can be obtained under appropriate processing conditions, especially by briefly keeping the temperature in the range of 100 - 120 °C, as partially crystalline polymers with a glass [transition] temperature of 50 to 55 °C and a crystallite melting point of approximately 175 °C. Copolymers with a slower rate of crystallization and reduced crystalline fraction can be obtained by addition of DL- or DD-lactide to L-lactide, or of DL- or LL-lactide to D-lactide: the melting point decreases, but the glass transition temperature remains the same. However, if the glass temperature is to be lowered, then a copolymerization with the cyclic glycolide is performed. The homopolymeric polyglycolide has a glass temperature of 20 to 25 °C. Thus, by copolymerizing appropriate fractions of lactide and glycolide, it is possible to adjust the glass temperature between approximately 20 and 55 °C.

The glass temperature of polylactide has a special role in the composting of the polymer and in its resorption into body tissues. The material is degraded in a first step by non-specific hydrolysis of the polyester chain. In a second step, the lactic acid formed is decomposed by micro-organisms, or enzymatically. The non-specific ester hydrolysis, which depends on the polymer's glass temperature, is rate-determining. 5 to 10 K above the glass temperature, the rate is higher by a factor of approximately 100 than at 5 to 10 K below the glass temperature.

Thus, the rate of degradation can be modified by establishing the glass temperature: depending on whether a fast or slow resorption in living human tissue is desired, for instance, a copolymer of lactide and glycolide with a glass temperature below or above 37 °C, respectively, would be used.

Poly lactide and especially, homopolymeric polylactide, is gaining increased attention also as degradable packaging material. It is essential, to this end, that the temperature of the fast-composting plants in general remain above 50 °C for longer periods of time.

To manufacture all kinds of moldings, or packaging materials such as films, bottles, deep-drawn cups or injection-molded items, it is necessary to melt the solid polymers and press the melt into molds through nozzles, or to manufacture sheets. To accomplish this, on the one hand the melt must be as flowable as possible. In accordance with an as yet unpublished proposal, by extension during solidification, it is possible to foster crystallization and thereby achieving a rigidity of over 3,000 N/mm<sup>2</sup>.

On the other hand, in the processing range between the glass temperature and the crystallite melting point, the mass should exhibit the highest possible melt rigidity and the melt rigidity should depend as little as possible on temperature changes. This is important, because during orientation and crystallization - which last no longer than a few tenths of a second to a few

seconds - the heat released can be removed only with difficulty. Experience shows that the material is heated by up to 35 °C. This has the consequence, for instance, that during so-called stretch-blow molding, uneven forming can occur.

Thus, even blowing assumes an only small dependence of the melt rigidity on the temperature. Otherwise, at a location with locally increased extension, the rise in temperature would cause a rapid drop in melt rigidity and thereby, overstretching at that location.

Known polylactide molding materials cause difficulties during processing, because of their excessively low melt rigidity.

In principle, melt rigidity can be influenced via the molecular weight distribution; this requires knowing in advance that:

the polyglycolide and polylactide are obtained by ring-opening melt polymerization, initiated with metal oxides or metal carboxylates.

The absolute configuration is retained, during polymerization, i.e., for instance in the polymerization of L-lactide, a pure poly-L-lactide is obtained. Statistical copolymerides are formed from mixtures of lactide stereoisomers and/or with glycolide. During initiation with, for instance, tin(II) octoate, the polymerization temperature should lie above the polymer's melting point and, depending on composition, will vary between 150 and 240 °C.

However, transesterification during polymerization will broaden the molecular weight distribution. Thus US-PS 4,719,246 describes the transesterification between two polylactides consisting of different enantiomers. After repeated heating and cooling for 10 to 60 minutes, a random distribution of chain elements is observed in the previously separated polymers. According to the US-PS, lactide-glycolide copolymers are obtained only after transesterification at 220 °C, for 2 h. However, since polymerization is terminated after a total residence time of 30 to 60 min, transesterification to an equilibrium distribution can not be completed in that time.

Hence the task exists of producing lactide polymers with a favorable processing behavior, in the sense mentioned earlier.

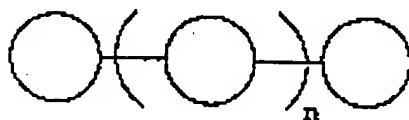
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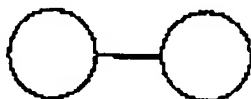
The task according to the invention is solved by manufacturing a polylactide with a certain fraction of long-chain branchings. That is, a corresponding fraction of chain molecules have branching points. According to the invention, the introduction of long-chain branchings more than compensates for the described disadvantages of the state of the art. It has proven advantageous for the fraction of branched molecules to be between 0.01 and 1.5 mol-%, preferably 0.1 to 0.3 mol-%.

Branches are obtained by mixing polymerizable, annular monomers in the

sense of polymerization, with bi- or higher-functional monomers of the type



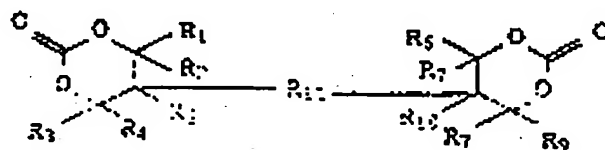
with bifunctional monomers of the type



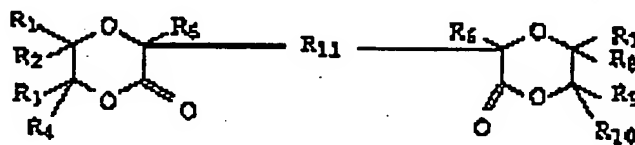
preferred, for reasons of accessibility and the need to avoid crosslinking as much as possible.

The annular molecular structures indicated above as circles correspond to the ring or rest accessible to ring-opening polymerization, for instance, the lactide 1,3-dioxan-2-one, or lactone.

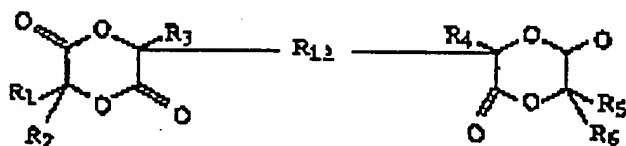
More specifically we refer to di-1,3-dioxan-2-one of the structure



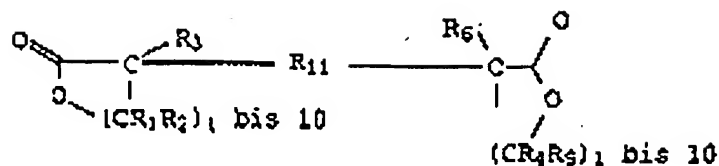
di-1,4-dioxan-2 one of the structure



lactides of the structure



or lactones of the structure



[KEY: bis = to]

as well as other potentially bifunctional annular compounds, in the sense of lactide polymerization.

In the structural formulas shown, the rests  $R_1$  through  $R_{12}$  can be the same or different, and can be hydrogen, branched or linear alkyl, alkene or alkylidene group with 1 to 12, preferably 1 to 4 carbon atoms, possibly substituted with halogen, hydroxy, alkoxy, formyl, acyl, amino, alkylamino, dialkylamino or cycloalkyl groups.

The rest  $R_{11}$  that connects the polymerizable rings, can be a linear or branched alkene or cycloalkene, such that the distance between the two rings is at least that necessary to build 2, preferably 4 to 10 carbon atoms in linear arrangement.

The branching monomers are added to monofunctional monomers and polymerization is performed in the customary manner. The fraction of branched monomers can be, for instance, 0.01 to 1.5 mol-%.

They can be obtained in accordance with the usual synthesis principles of organic chemistry, which are obvious to the professional from the constitutional formula.

#### Comparison test with a linear polylactide

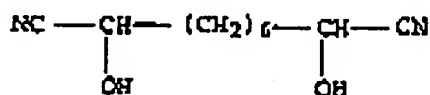
1.4 kg L-lactide (100 mol) are melted under argon in a stirrer vessel at 120 °C and then reacted with 0.01 mol 2-ethyl-tin(II)-hexanoate as initiator, dissolved in toluene. The monomer is further heated and polymerized at 190 °C for 60 minutes. The melt is pressed through a nozzle at the bottom of the stirrer vessel and the strand so obtained is chilled to an amorphous material in a water bath and then granulated. The granulate is dried at 110 °C for 20 hours, under reduced pressure (approximately 5 mbar), where it crystallizes. The inherent viscosity, measured in a 0.1 % solution in chloroform at 25 °C, is 1.58 dl/g. The dry granulate is melted at 205 °C in an injection molding machine and the melt is elaborated to amorphous cups, in a mold cooled to 25 °C. The conical cups have an opening of 58 mm diameter, a bottom of 45 mm diameter, a height of 5 mm and a wall thickness of 1.6 mm.

The cups serve as parisons in a stretch-blow molding test. They are fixed by their opening in a gas pressure-tight device and then heated with this device in a circulating air oven for two minutes at 98 - 100 °C. Next they are connected to a compressed air source and blown at a pressure of approximately 0.8 bar. It was seen that blisters form in the cup wall, of 1 to 3 cm in size, which burst, while the rest of the cup remains nearly unstretched.

The results did not improve even after varying the temperature and the blowing pressure.

### Example

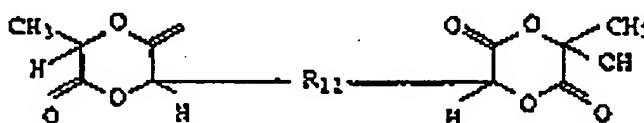
The dicyanogen hydriene



is obtained from octanedial-1,6 - molecular weight 142.2 g/mol, boiling point 97 °C at 4 mbar - by addition of hydrocyanic acid. The corresponding  $\alpha,\omega$ -dihydroxycarboxylic acid is obtained by saponification and then mixed with a 10 molar excess of L-lactic acid and esterified with n-octanol. After addition of 0.1 % titanium tetrabutylate as transesterification catalyst, the octyl ester is heated to 240 °C and n-octanol is distilled off, while stirring.

The residue consists essentially of L-lactide, containing approximately 10 mol-% of the compound

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where  $R_{11} = -(\text{CH}_2)_6-$ .

Follow the procedure described in the comparison example, except that 0.008 mol of branching agent are added, per mol of L-lactide. Poly-L-lactide with an inherent viscosity of 1.55 [dl/g] is obtained and elaborated into the cups described.

After heating to 98 - 100 °C, the cups are blown at a pressure of approximately 0.8 bar; without bursting, they are shaped into nearly spherical constructs of 8 to 20 cm in diameter and a wall thickness of 0.1 mm.

#### **Patent claims**

1. Polylactide homo and copolymers containing long-chain branchings.
2. Polylactide according to claim 1, as obtained by ring-opening polymerization of the corresponding monomers, in the presence of monomers acting multifunctionally, with respect to polymerization.
3. Polylactide according to claim 2, obtained by polymerization in presence of 0.01 to 0.3 mol-% of the multifunctional monomer.
4. Polylactide according to claim 1, containing units of a bifunctional, branched monomer.
5. Polylactide according to claim 1, containing a di-1,3-dioxan-2-one, a di-1,4-dioxane-2-one, a dilactide, or a dilactone, as branching monomer.

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RELEVANT DOCUMENTS

Categ	Identification of the document with indication, where necessary, of the relevant part	Ref. to Claim	APPLIC. CLASSIF. (Int.Cl.5)
X	EP-A-0 314 245 (C. C. A. BIOCHEM) * Claims 1 - 10 *	1-5	C08G63/08
A	EP-A-0 411 545 (ETHICON INC.)	1-5	
A	EP-A-0 261 470 (AMERICAN CYANAMID COMPANY)	1-5	
A	EP-A-0 098 394 (AMERICAN CYANAMID COMPANY)	1-5	
		1	RESEARCHED TOPICS (Int.Cl.5) C08G

This research report was prepared for all patent claims

Research site THE HAGUE	End of research date 14 Dec 94	Official examiner Andriollo, G
CATEGORY OF DOCUMENTS LISTED		T: theory or principles on which the invention rests
X: of special importance by itself		E: old patent, but published only on or after the application date
V: of special importance in combination with another application of the same category		D: document listed in the application
A: technological background		L: document listed for other reasons
O: not written disclosure		A: Member of the same patent family, concurring document
P: intermediate literature		